



## PATENT ABSTRACTS OF JAPAN

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## (54) RUBBER COMPOSITION FOR STUDLESS TIRE

## (57) Abstract:

**PROBLEM TO BE SOLVED:** To obtain the subject composition for a studless tire having increased frictional force on a frozen or snowy road to improve the running performance of the tire on the road of the above condition by compounding a diene rubber with rice bran ceramic particles at a specific ratio.

**SOLUTION:** This composition is produced by compounding (A) a diene rubber, (B) a carbon black (preferably having a nitrogenadsorption specific surface area  $N_2SA$  of 1-200 $m^2/g$  and a DBP oil absorption of

80-150 $mL/1.00g$ ) and further (C) an inorganic reinforcing filler such as silica and (D) an oil, etc., and compounding the obtained rubber composition with (E) 1-10 pts.wt. (based on 100 pts.wt. of the component A) of a rice bran ceramic. The component E can be produced e.g. by carbonizing defatted rice bran at a high temperature optionally after impregnating with a resin having a condensed polycyclic aromatic structure such as a phenolic resin. The component E preferably has a representative average particle diameter of 50-500 $\mu m$  and a Vickers hardness of 100-400 on an average.

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(54)【発明の名称】 スタッドレスタイヤ用ゴム組成物

(57)【要約】

【課題】 タイヤの氷雪路上性能、特に氷雪路上摩接力を向上させたスタッドレスタイヤの製造に使用するのに適したスタッドレスタイヤ用ゴム組成物を提供する。

【解決手段】 ジエン系ゴム100重量部に対し米ぬかセラミックス粒子1〜10重量部を配合して成るスタッドレスタイヤ用ゴム組成物。

## 【特許請求の範囲】

【請求項1】 ジエン系ゴム100重量部に対し米ぬかセラミックス粒子1〜10重量部を配合して成るスタッドレスタイヤ用ゴム組成物。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明はスタッドレスタイヤ用ゴム組成物に関し、更に詳しくは氷雪路上の摩擦力の向上したスタッドレスタイヤ用ゴム組成物に関する。

【0002】

【従来の技術】タイヤの氷雪路上走行用としてスパイクタイヤの使用やタイヤへのチェーン装着が行われてきたが、これらは粉塵発生という環境問題を惹き起すため、これらに代る氷雪路上走行用タイヤとしてスタッドレスタイヤが開発されてきた。スタッドレスタイヤは、一般に凍結路面では一般路面での摩擦係数の1/10程度まで低下して滑りやすくなっているため、タイヤの摩擦力を高くするよう材料面及び設計面から工夫がなされている。材料面からいえば低温でも硬くなりにくい低温特性の良好なゴムが開発されてきた。しかしながら、スパイクタイヤに比較して、スタッドレスタイヤの氷雪路上性能は未だ十分とはいえず、一層の改良が望まれている。

【0003】

【発明が解決しようとする課題】従って、本発明の目的はスタッドレスタイヤの氷雪路上摩擦力を高くしてスタッドレスタイヤの氷雪路上性能を向上させることのできるタイヤトレッド用ゴム組成物を提供することにある。

【0004】

【課題を解決するための手段】本発明に従えば、ジエン系ゴム100重量部に対し米ぬかセラミックス粒子1〜10重量部を配合して成るスタッドレスタイヤ用ゴム組成物が提供される。

【0005】

【発明の実施の形態】本発明に従えば、スタッドレスタイヤ、特にそのトレッド部に使用するゴム組成物として、従来のスタッドレスタイヤ用ゴム組成物に一般的に使用されているジエン系ゴム、カーボンブラック（好ましくは窒素比表面積 $N_2$  SA 70〜200 $m^2/g$ 、DBP吸油量80〜150 $ml/100g$ ）、更にはシリカ、炭カルなどの無機補強充填剤、オイルなどを配合したゴム組成物に米ぬかセラミックスを配合することにより、表面粗さが増すことによる除水、排水効果と硬質物質配合によるエッジ効果（堀り起し効果）が得られ、氷雪路上摩擦力を高めることができる。

【0006】本発明に用いられるジエン系ゴムとしては、例えば、天然ゴム（NR）、ポリイソプレンゴム（IR）、各種スチレン-ブタジエン共重合体ゴム（SBR）、各種ポリブタジエン（BR）などをあげることができ、特に低温性能を考慮すれば天然ゴムを少なくと

も40重量部以上とした他のジエン系ゴムとのブレンドゴムの使用が好ましい。

【0007】本発明に従えば、前記ジエン系ゴム100重量部に対し、米ぬかセラミックス粒子1〜10重量部、好ましくは1〜3重量部を配合することによってゴム表面に形成する凹凸が、氷雪路上に発生する水をトラップ又は除去する効果が得られ、着着摩擦によって氷雪路上摩擦力が向上する。米ぬかセラミックス粒子の配合量がジエン系ゴム100重量部当り1重量部未満では水のトラップ又は除去に必要な表面凹凸が形成されないもので好ましくなく、逆に10重量部を超えると、タイヤ表面の氷雪路面への接地面積が低下するので好ましくない。

【0008】本発明のゴム組成物に配合される米ぬかセラミックス粒子は、例えば脱脂した米ぬかを直接又はフェノール樹脂のような縮合多環芳香族構造を有する樹脂を含浸させた後、高温で焼成して炭素化させることによって得られるもので、例えばフェノール樹脂を含浸させたものは例えば窒素雰囲気下で700〜1,100℃で焼成することにより硬質の多孔炭化粒子を得ることができる。好ましい米ぬかセラミックス粒子の代表平均粒径は50〜500 $\mu m$ で、好ましい硬度はビッカース硬度で平均100〜400である。

【0009】本発明に従ったスタッドレスタイヤ用ゴム組成物にはジエン系ゴムに加えて、補強性充填剤、硫黄、加硫促進剤、老化防止剤、充填剤、軟化剤、可塑剤などのタイヤ用に一般に配合されている各種添加剤や特殊配合剤例えばゴム成分としてではなく、可塑剤成分としての低分子量ポリマー（重量平均分子量1,000〜60,000）や低硬度ゴム、短繊維などを配合することができ、かかる配合物は一般的な方法で加硫してタイヤトレッドを製造することができる。これらの汎用添加剤の配合量も一般的な量とすることができる。

【0010】

【実施例】以下、実施例及び比較例によって本発明を更に説明するが、本発明の範囲をこれらの実施例に限定するものでないことは言うまでもない。

【0011】実施例1〜5及び比較例1〜2

表1に示す配合内容（重量部）でそれぞれの成分を配合し、加硫促進剤と硫黄を除く原料ゴム及び配合剤を1.7リットルのパンバリーミキサーで5分間混合した後、この混合物に加硫促進剤と硫黄とを8インチの試験用練りロール機で4分間混練し、ゴム組成物を得た。これらのゴム組成物を160℃で20分間プレス加硫して、目的とする試験片を調製し、その氷上摩擦係数を測定した。得られた加硫物の氷上摩擦試験結果は表1に示す通りである。

【0012】

【表1】

表 1

	比較例 1	実施例 1	実施例 2	実施例 3	実施例 4	比較例 2	実施例 5
NR**	80	80	60	60	60	60	60
BR**	40	40	40	40	40	40	40
CB**	55	55	55	55	55	55	55
液状ポリマー**	15	15	15	15	15	15	15
7070カド	15	15	15	15	15	15	15
至給導	3	3	3	3	3	3	3
2777 酸	1	1	1	1	1	1	1
老化防止剤**	1	1	1	1	1	1	1
ワックス	1	1	1	1	1	1	1
硬 質	1.5	1.5	1.5	1.5	1.5	1.5	1.5
加硫促進剤**	1.2	1.2	1.2	1.2	1.2	1.2	1.2
米ぬかセラミックスBC900**	-	1	2.5	5	10	25	-
米ぬかセラミックスES900**	-	-	-	-	-	-	2.5
氷上摩接係数							
10km/hr	100	103	105	101	100	77	107
15km/hr	100	108	108	105	105	80	108
20km/hr	100	110	110	108	107	84	105
25km/hr	100	113	113	110	110	89	100

\*1: TTE20

\*2: NIPOL 1220 日本ゼオン (株)

\*3: SBRBLACK R220 昭和キャボット (株)

\*4: Polyoil 130 日本ゼオン (株) (液状BR、重量平均分子量15000、シス含量60%)

\*5: アンチゲン 6 C 住友化学工業 (株)

\*6: ノクセラール MS-F 大内新興化学 (株)

\*7: 炭化した米ぬかにフェノール樹脂を含有 (含炭量=25重量部/米ぬか 100重量部) した後、N<sub>2</sub>雰囲気中 900℃で4時間焼成して得られた硬く高強度の粒子 (平均粒子径約 300μm)。

\*8: フェノール樹脂を含有させた以外は\*7に同じ。

【0013】なお氷上摩接試験方法は、温度制御された恒温室内に設置された氷面上にゴム試験片を一定荷重で押し付け、一定速度で滑らせる時の抵抗 (摩接力) を検出することによって行われる。実施例及び比較例に示した氷上摩接試験条件は、氷温-3℃、速度10~25km/hr、試験片には接地圧力が3kg/cm<sup>2</sup>となるように荷重をかける。結果は表1に示した通りである。なお結果\*

\*は比較例1の値を100として指数表示した。

【0014】

【発明の効果】以上説明したように、本発明に従ってジエン系ゴムに米ぬかセラミックスを配合することにより、氷上摩接力の著しい向上が認められ、スタッドレスタイヤ用ゴム組成物として最適である。

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TITLE: RUBBER COMPOSITION FOR STUDLESS TIRE  
PUBN-DATE: August 18, 1998

INVENTOR-INFORMATION:

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APPL-NO: JP09025486

APPL-DATE: February 7, 1997

INT-CL (IPC): C08L009/00, C08K003/00

ABSTRACT:

PROBLEM TO BE SOLVED: To obtain the subject composition, for a studless tire having increased frictional force on a frozen or snowy road to improve the running performance of the tire on the road of the above condition by compounding a diene rubber with rice bran ceramic particles at a specific ratio.

SOLUTION: This composition is produced by compounding  
(A) a diene rubber,  
(B) a carbon black (preferably having a nitrogenadsorption specific surface area  $N_{SB} > 2 < /SB > S_A$  of 1-200m<sup>2</sup>/g and a DBP oil

absorption of  
80-150mL/1.00g) and further (C) an inorganic reinforcing  
filler such as silica  
and (D) an oil, etc., and compounding the obtained rubber  
composition with (E)  
1-10 pts.wt. (based on 100 pts.wt. of the component A) of a  
rice bran ceramic.  
The component E can be produced e.g. by carbonizing  
defatted rice bran at a  
high temperature optionally after impregnating with a resin  
having a condensed  
polycyclic aromatic structure such as a phenolic resin.  
The component E  
preferably has a representative average particle diameter  
of 50-500 $\mu$ m and a  
Vickers hardness of 100-400 on an average.

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(71)Applicant : YOKOHAMA RUBBER CO  
LTD:THE

(22)Date of filing : 07.02.1997

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PROBLEM TO BE SOLVED: To obtain the subject composition for a studless tire having increased frictional force on a frozen or snowy road to improve the running performance of the tire on the road of the above condition by compounding a diene rubber with rice bran ceramic particles at a specific ratio.

SOLUTION: This composition is produced by compounding (A) a diene rubber, (B) a carbon black (preferably having a nitrogen adsorption specific surface area N<sub>2</sub>SA of 1-200m<sup>2</sup>/g and a DBP oil absorption of 80-150mL/1.00g) and further (C) an inorganic reinforcing filler such as silica and (D) an oil, etc., and compounding the obtained rubber composition with (E) 1-10 pts.wt. (based on 100 pts.wt. of the component A) of a rice bran ceramic. The component E can be produced e.g. by carbonizing defatted rice bran at a high temperature optionally after impregnating with a resin having a condensed polycyclic aromatic structure such as a phenolic resin. The component E preferably has a representative average particle diameter of 50-500µm and a Vickers hardness of 100-400 on an average.

## LEGAL STATUS

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the rubber constituent for studless tires whose still more detailed frictional force snow-and-ice on the street improved about the rubber constituent for studless tires.

[0002]

[Description of the Prior Art] Although use of a spike tire and chain wearing into a tire have been performed as an object for snow-and-ice on-the-street transit of a tire, in order that these may cause the environmental problem of dust generating, the studless tire has been developed as a tire for snow-and-ice on-the-street transit replaced with these. Since a studless tire falls on a freezing road surface to about [ of coefficient of friction in a general road surface ] 1/10 and it has generally slipping-come to be easy of a studless tire, the device is made from the material side and the layout side so that frictional force of a tire may be made high. If it says from a material side, rubber with the good low-temperature property which cannot become hard easily at low temperature will have been developed. However, as compared with the spike tire, it cannot say that the snow-and-ice engine performance of a studless tire on the street is still enough, but much more amelioration is desired.

[0003]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is to offer the rubber constituent for tire treads which can make high snow-and-ice frictional force of a studless tire on the street, and can raise the snow-and-ice engine performance of a studless tire on the street.

[0004]

[Means for Solving the Problem] If this invention is followed, a rubber constituent for studless tires which blends the rice bran ceramic particle 1 - 10 weight sections, and changes to the diene system rubber 100 weight section will be offered.

[0005]

[Embodiment of the Invention] If this invention is followed, as a studless tire and a rubber constituent used especially for the tread section The diene system rubber currently generally used to the conventional rubber constituent for studless tires, carbon black (desirable -- nitrogen specific-surface-area N2 SA 70-200m<sup>2</sup> / g --) By blending the rice bran ceramics with the DBP oil absorption of 80-150ml / rubber constituent which blended further inorganic reinforcing fillers, such as a silica and calcium carbonate, 100g of oil etc., etc. Dewatering by surface roughness increasing, the wastewater effect, and the edge effect (\*\*\*\*\* (ing) effect) by hard material combination are acquired, and snow-and-ice frictional force on the street can be heightened.

[0006] If natural rubber (NR) (polyisoprene rubber IR) various styrene-butadiene copolymer rubber (SBR), various polybutadienes (BR), etc. can be raised and especially low-temperature-performance ability is taken into consideration as diene system rubber used for this invention, for example, use of blend rubber with other diene system rubber which carried out natural rubber to more than 40 weight sections at least is desirable.



[0007] If this invention is followed, a trap or the effect to remove will be acquired to said diene system rubber 100 weight section in the water which the rice-bran ceramic particle 1 - 10 weight sections, and the irregularity formed in the rubber surface by blending 1 - 3 weight section preferably generate in a snow-and-ice on the street, and snow-and-ice frictional force on the street will improve by adhesion friction. Since the trap of water or surface irregularity required for removal is not formed under in 1 weight section, if the loadings of a rice bran ceramic particle exceed 10 weight sections conversely preferably per diene system rubber 100 weight section, since the crawler bearing area to the snow-and-ice road surface on the surface of a tire will fall, it is not desirable.

[0008] After the rice bran ceramic particle blended with the rubber constituent of this invention carries out impregnation of the resin which has condensation polycyclic aromatic series structure like direct or phenol resin for the rice bran degreased, for example, it is obtained by making it calcinate and carbonize at an elevated temperature, and that to which impregnation of the phenol resin was carried out can obtain a hard porosity carbonization particle by calcinating at 700-1,100 degrees C for example, under nitrogen-gas-atmosphere mind. The representation mean particle diameter of a desirable rice bran ceramic particle is 50-500 micrometers, and a desirable degree of hardness is an average of 100-400 in Vickers hardness number.

[0009] It adds to the rubber constituent for studless tires according to this invention at diene system rubber. It is not as the various additives generally blended with tires, such as a reinforcement nature bulking agent, sulfur, a vulcanization accelerator, an antioxidant, a bulking agent, a softener, and a plasticizer, or a special compounding agent, for example, a rubber component. The low-molecular-weight polymer (weight average molecular weight 1,000-60,000) as a plasticizer component, low degree-of-hardness rubber, a staple fiber, etc. can be blended, and this compound is vulcanized by the general method and can manufacture a tire tread. The loadings of these general-purpose additives can also be made into a general amount.

[0010]

[Example] It cannot be overemphasized that it is not what limits the range of this invention to these examples hereafter although an example and the example of a comparison explain this invention further.

[0011] After blending each component from the contents of combination (weight section) shown in examples 1-5 and the example 1 of a comparison - the 2 table 1 and mixing the raw material rubber and the compounding agent except a vulcanization accelerator and sulfur for 5 minutes with a 1.7l. Banbury mixer, a vulcanization accelerator and sulfur were kneaded for 4 minutes with the 8 inches mixing mill for a trial into this mixture, and the rubber constituent was obtained. Press cure of these rubber constituents was carried out for 20 minutes at 160 degrees C, the target test piece was prepared, and the Hikami coefficient of friction was measured. The Hikami friction test result of the obtained vulcanizate is as being shown in Table 1.

[0012]

[A table 1]

表 1

	比較例 1	実施例 1	実施例 2	実施例 3	実施例 4	比較例 2	実施例 5
NR*	60	60	60	60	60	60	60
BR*	40	40	40	40	40	40	40
CB*	55	55	55	55	55	55	55
縮状ポリマー**	15	15	15	15	15	15	15
7070シリカ	15	15	15	15	15	15	15
亜鉛華	3	3	3	3	3	3	3
スズン酸	1	1	1	1	1	1	1
老化防止剤*	1	1	1	1	1	1	1
ワックス	1	1	1	1	1	1	1
硫黄	1.5	1.5	1.5	1.5	1.5	1.5	1.5
加硫促進剤*	1.2	1.2	1.2	1.2	1.2	1.2	1.2
米ぬかセラミックスRBC900*	-	1	2.5	5	10	25	-
米ぬかセラミックスRBC900**	-	-	-	-	-	-	2.5
氷上摩擦係数							
10km/hr	100	103	105	101	100	77	107
15km/hr	100	108	108	105	105	80	106
20km/hr	100	110	110	108	107	84	105
25km/hr	100	113	118	110	110	89	100

\*1: TTR20

\*2: NIPOL 1220 日本ゼオン(株)

\*3: SHOBLOCK N220 昭和キャボット(株)

\*4: Polyoil 130 日本ゼオン(株)(液状BR、重量平均分子量15000、シス含量80%)

\*5: アンチゲン6C 住友化学工業(株)

\*6: ノクセラー NS-F 大内新興化学(株)

\*7: 脱脂した米ぬかにフェノール樹脂を含浸(含浸量=25重量部/米ぬか 100重量部)した後、N<sub>2</sub>雰囲気中 900°Cで4時間焼成して得られた硬く高強度の粒子(平均粒子径約 300μm)。

\*8: フェノール樹脂を含浸させた以外は\*7に同じ。

[0013] In addition, the Hikami friction test method pushes a rubber test piece by the fixed load on the surface of ice installed in the thermostatic chamber by which temperature control was carried out, and is performed by detecting the resistance (frictional force) when letting it slide in constant speed. For the Hikami friction test conditions shown in the example and the example of a comparison, in the ice temperature of -3 degrees C, speed 10 - 25 km/hr, and a test piece, the ground pressure force is 3kg/cm<sup>2</sup>. A load is applied so that it may become. A result is as having been shown in Table 1. In addition, the result set the value of the example 1 of a comparison to 100, and indicated by the characteristic.

[0014]

[Effect of the Invention] As explained above, by blending the rice bran ceramics with diene system rubber according to this invention, the remarkable improvement in the Hikami frictional force is accepted, and it is the optimal as a rubber constituent for studless tires.

[Translation done.]

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